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# 1

# Crystal Lattice Imaging Using Atomic Force Microscopy

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## 1. Introduction

Atomic force microscopy (AFM) has been a very useful tool in interrogating the micron-to-nano sized structures at both atomic and subnanometer resolution. AFM allows both imaging of surfaces and interactions with surfaces of interest to help researchers explain the crystal lattice structure, and surface chemical and mechanical properties at nano scale. Since the invention of AFM, one has been frequently attracted by AFM images when browsing through many scientific publications in physics, chemistry, materials, geology, and biology (Gan, 2009; Sokolov *et al.*, 1999; Wicks *et al.*, 1994). AFM has been successfully used for imaging solid surfaces with subnanometer resolution for natural materials such as minerals, synthetic materials such as polymers and ceramics, and biological materials such as live organisms. There are also numerous reports of molecular and subnanometer resolution on biological and polymer samples.

Atomic force microscopy (AFM) has been quite successfully used by scientists and researchers in obtaining the atomic resolution images of mineral surfaces. It is quite amazing to see the individual atoms, and their arrangements, that make up the surfaces. In some cases, atoms from the mineral surfaces can be deliberately removed with the AFM so that the internal structure of the surface can be studied.

The key to obtaining atomic-scale imaging is precisely control the interactions between the atoms of the scanning tip and the atoms of the surface being studied. Ideally a single atom of the tip is attracted or repelled by successive atoms of the surface being studied. However, this is a dynamic environment and there can be accidental or deliberate wear of the tip and the surface, so the situation is far from ideal. A number of theoretical and practical studies have added some understanding of this interaction but our understanding is still incomplete (Nagy, 1994). Despite the imperfect knowledge, application of the instrument to mineral studies demonstrates that the AFM works well, often at atomic scale resolution.

It is now well established with some success that AFM can also be used to investigate the crystal lattice structure of mineral surfaces. Atomic resolution has been successfully obtained on graphite (Albrecht & Quate, 1988; Sugawara *et al.*, 1991), molybdenum sulfide (Albrecht & Quate, 1988), boron nitride (Albrecht & Quate, 1987), germanium (Gould *et al.*, 1990), sapphire (Gan *et al.*, 2007), albite (Drake & Hellmann, 1991), calcite (Ohnesorge & Binnig, 1993) and sodium chloride (Meyer & Amer, 1990). The AFM has also been used to

investigate the crystal lattice structure of the tetrahedral layer of clay minerals in 2:1 layer structures, such as muscovite (Drake *et al.*, 1989), illite (Hartman *et al.*, 1990) and montmorillonite (Hartman *et al.*, 1990). Atomic-scale resolution has also been obtained for the basal oxygen atoms of a mixed-layered illite/smectite (Lindgreen *et al.*, 1992), zeolite clinoptilolite (Gould *et al.*, 1990) and hematite (Johnsson *et al.*, 1991).

Wicks *et al.* (Wicks *et al.*, 1992) were probably the first to simultaneously report the surface images of both the tetrahedral and octahedral sheets of lizardite (1:1 layer structure) using AFM, and they identified the surface hydroxyl groups and magnesium atoms in the octahedral sheet. In this way, they identified the two sides of the lizardite clay mineral. The surface images of chlorite (2:1:1-type structure) were also investigated by AFM, and both the tetrahedral sheet and the brucite-like interlayer sheet were observed (Vrdoljak *et al.*, 1994). Recently, Kumai *et al.* (Kumai *et al.*, 1995) examined the kaolinite surface using AFM. They used the "pressed" powder sample preparation technique, and obtained the surface images of both the silica tetrahedral surface and alumina octahedral surface of kaolinite particles.

Despite great success in obtaining atomic resolution, AFM images may be subject to various distortions, such as instrumental noise, drift of the piezo, calibration problem with the piezo, vibrations, thermal fluctuations, artifacts created by the AFM tip, contamination of the mineral or tip surface, and tip induced surface deformations. The initial AFM images are often noisy and suffer from instrumental effects such as image bow due to sample tilt. Some of these problems can be fixed with data processing software by applying appropriate flattening, filter out low frequency noise, and clarify the structural details in an image using two dimensional fast-Fourier transforms (2DFFT). Some of these fixtures will be discussed in the subsequent section of this chapter by following a case study on obtaining crystal lattice images of kaolinite. Similar experimental routine could be applied on obtaining atomic resolution images of any surface of interest.

This chapter summarizes the achievement of AFM to obtain atomic resolution images of mineral surfaces. In particular, a case study for obtaining crystal lattice images on kaolinite surface will be presented. The principles of AFM and its different modes of operation will be introduced. A brief introduction of image acquisition and filtering routines will be discussed followed by tip and surface interaction. This will be followed by different ways to acquire images with atomic resolution. The important issues of reproducibility and artifacts will be discussed. A critical review of literature will be supplemented in each section for obtaining atomic resolution images. Finally, the new challenges for AFM to obtain atomic resolution images on the complex surfaces will be discussed.

## 2. Basic principles and operation modes of AFM

### 2.1 Principles of AFM

An AFM consists of a probe, scanner, controller, and signal processing unit-computer. AFM works by rastering a sharp probe across the surface to obtain a three-dimensional surface topograph. As the probe rasters, it feels the highs and lows of surface topography through complex mechanisms of tip-surface interactions. These signals are sent back via a laser reflected back from the probe surface to a photo-detector. The photo-detector through a feedback control loop, keep the tip at constant height or constant force from the surface. The

feedback signals are sent to a signal processing software, which generates a three-dimensional topograph of the surface.

### 2.2 Operation modes of AFM

The operating modes of AFM can be divided *into static* (*DC*) *mode* – the probe does not vibrate during imaging, and *dynamic* (*AC*) *mode* – the cantilever is excited to vibrate at or off its resonant frequency. The dynamic mode AFM can be either an amplitude-modulated AFM (AM-AFM) or a frequency-modulated AFM (FM-AFM). Usually, AM-AFM is referred to as intermittent contact mode or tapping mode. The imaging could be conducted by manipulating the repulsive interaction between a probe and the surface, which is referred to as contact mode imaging. When the probe images the surface with an attractive interaction, is usually referred to as non-contact mode. Note that both the DC and AC modes may be operated in contact mode; in most cases, however, DC mode is referred to as contact mode. FM-AFM is usually referred as non-contact mode.

#### 2.2.1 Contact mode

The contact mode can be operated in constant force mode or constant height mode, depending on whether the feedback loop is turned on. *Constant force* requires a setpoint that needs to be manually adjusted to compensate for the drift during imaging or to control the tip-surface force. This is done on non-atomically smooth surface. The piezo-drive signal is used for generating the height signal on a topograph. *Constant height* mode is most suitable for scanning atomically smooth surfaces at a fixed setpoint (tip-surface force). The deflection of the cantilever is used for generating the height signal on a topograph.

#### 2.2.2 Intermittent or tapping mode

The intermittent or tapping mode (or AM-AFM) is usually conducted on soft samples, such as loosely attached structure on the surface or even more delicate biological samples such as DNA, cells and micro-organisms. The probe is excited at a setpoint amplitude of cantilever oscillation. The amplitude of the cantilever dampens from full oscillation (non contact) to smaller oscillations when it encounters a structure on the surface (intermittent contact). The change in the amplitude of the probe stores the structural information of the surface, which generates a three-dimensional topograph. A large setpoint amplitude is required in the noncontact region, and a small setpoint amplitude is required in the intermittent contact regime. For example, Gan (Gan, 2009) pointed out that the Magonov group achieved molecular resolution with AM-AFM (Belikov & Magonov, 2006; Klinov & Magonov, 2004) and the Engel group achieved subnanometer resolution on protein samples (Moller *et al.*, 1999).

#### 2.2.3 Non-contact mode

Martin *et al.* (Martin *et al.*, 1987) introduced the concept of non-contact mode (FM-AFM) in 1987 to precisely measure the interaction force between a probe and the surface. During non-contact mode, the probe is excited to oscillate at its resonant frequency. The frequency shift of a probe is monitored, as it encounters a surface structure, which generates surface

topograph. Giessibl (Giessibl, 2000) was able to use an AFM in non-contact mode to obtain atomic resolution images of reactive surfaces such as Si.

## 3. Image acquisition and filtering

The quality of the raw data is of primary importance in obtaining high resolution AFM images. A good quality raw image must be obtained without the use of online filters. Special attention should be taken in order to determine if an image is of good quality for a particular sample and whether the image is real or not. This is done by varying scan direction and speed, varying instrumental gains and contact force, changing sample locations, retracting and extending the tip, and collecting multiple set of data from different sample and using different tips. Other factors such as varying color contrast/offset, z-height range, and checking for periodicity, by looking at the screen close up and from a distance, are important.

Once a good raw image has been obtained, some filtering can be applied to enhance the features seen in the image, and to distinguish between instrumental artifacts and real features. A filtered image should always be compared to the unfiltered image as a cross check to ensure that artifacts have not been introduced as a result of filtering.

A variety of data processing programs are available to filter images. These will vary from instrument to instrument and are explicitly described in the user's manual. Some of the commonly followed filter routines are described below.

### 3.1 Flattening

Flattening subtracts the average value of the height of each scan line from each point in the scan line and reduces the effect of image bow and vibration in the *Y* direction. This could be applied automatically during real time imaging or manually after the image is captured. At times, a plane is fitted to the captured image. Plane fit calculates a best fit second order polynomial plane, and subtracts it from the image. Usually this is applied once in *X* direction and once in *Y* direction

### 3.2 Low pass / high pass filters

Lowpass filtering replaces each data point in the image with a weighted average of the 3 x 3 cell of points surrounding and including the point. It may be applied a number of times. This removes the high frequency noise, but it also reduces image resolution by "defocusing" the periodic features observed in the raw data. Highpass filtering on the other hand replaces each data point with a weighted difference between the data point and each of its eight neighbors. This routine is particularly good for enhancing height differences within an image.

### 3.3 2-Dimensional Fast Fourier Transforms (2DFFT)

This is the most useful filtering routine which can greatly improve images. This technique converts the image to the frequency domain by calculating the 2-dimensional power spectrum or 2DFFT. The 2DFFT of the image may then be filtered and an inverse transform

performed on the filtered data to produce a new image. This routine should be practiced with care by resizing the image to the maximum pixel dimensions, prior to the application of the 2DFFT, and then varying color contrast/offset of the power spectrum image. Some criticism of this technique by AFM users were reported as (1) 2DFFT may introduce the features which are not present in the initial image, and (2) use of a 2DFFT smears the atomic positions so that the resolution of individual atom is not obtained. In first case, it's possible to introduce the artifacts after 2DFFT processing, and it's a matter of experience and competence in selecting or rejecting the right periodicities to obtain an image. In contradiction to the second criticism, Wicks *et al.* (Wicks *et al.*, 1994) successfully reported two different atomic–repeat units of lizardite in a single image during a high tracking force experiments. They demonstrated that this criticism of 2DFFT is not valid.

## 4. Resolution

AFM is a computer-controlled local probe technique which makes it difficult to give a straightforward definition of resolution. The AFM vertical resolution is mainly limited by thermal noise of the deflection detection system. Most commercial AFM instruments can reach a vertical resolution as low as 0.01 nm for more rigid cantilevers. The lateral resolution of AFM is defined as the minimum detectable distance between two sharp spikes of different heights. A sharp tip is critical for achieving high resolution images. Readers may refer to Gan (Gan, 2009) for more discussion on probe sizes.

Despite great success by researchers in obtaining atomic resolution images, AFM is looked at with doubt as compared to scanning tunneling microscopy. These doubts about resolution have been dispersed. For example, Ohnesorge and Binnig (Ohnesorge & Binnig, 1993) obtained images of the oxygen atoms standing out from the cleavage plane of calcite surface in water. Similarly, Wicks *et al.* (Wicks *et al.*, 1993) used high tracking force to strip away the oxygen and silicon of the tetrahedral sheet to image the interior O, OH plane of lizardite at atomic resolution. Recently, Gupta *et al.* (Gupta *et al.*, 2010) showed high resolution images of silica tetrahedral layer and alumina octahedral layer of kaolinite surface.

## 5. Tip-surface interaction

Tip-surface forces are of paramount importance for achieving high resolution AFM images. They can be described based on (i) continuum mechanics, (ii) the long range van der Waals force, (iii) the capillary force, (iv) the short range forces, (v) the electrical double layer force in a liquid, and (vi) contamination effects.

A continuum model treats the materials of the tip and sample as continuum solids. Various continuum models such the Hertz model, the JKR model, the MD model, and the Schwarz model consider mechanical deformation or surface energy alone or both. At high applied force, the tip and the substrate may deform inelastically. One should thus be cautious in using continuum models to predict tip-surface interactions. The van der Waals (vdW) force between macroscopic objects is due to the dispersion interactions of a large number of atoms between two objects interacting across a medium. The strength of the vdW force is measured with the Hamaker constant. The macroscopic vdW force is determined by the

properties of the materials and the medium, and the tip geometry. In most cases, vdW forces are attractive between tip and surface of interest. The capillary force arises when tip approaches the surface in air. The water molecules on the surface forms a bridge with the tip and an increased force must be applied in order to detach the tip from the surface. This increased force is called the capillary force, and depends on the surface properties, humidity, temperature and geometry of the tip. The capillary force is usually more long-ranged than the van der Wall force under moderate humidity conditions. Short-range forces become important when the tip-surface distance is less than 1 nm. Short-range force may originate from Born repulsion, chemical bonding, and electrostatic and vdW interactions between atoms. The electrical double layer force arises when two surfaces approach each other in solution. The surfaces develop charges either by protonation/de-protonation, adsorption, and specific chemical interaction, which attracts counterions and co-ions from solution. Lastly, contaminants, particularly organic materials adheres either to surface or tip, even in trace amounts, can significantly affect the tip-surface interaction. Therefore, a clean tip and surface are highly desirable prior to and throughout the experiments. This is a brief review of tip-surface interactions, and readers are advised to review classic textbooks (Butt *et al*., 2003; Israelachvili, 1985; Masliyah & Bhattacharjee, 2006).

In order to achieve atomic resolution image, the external load on the tip must counteract the tip-surface interactions discussed above. The external load is a function of spring constant of the tip and its bending. It is highly desirable to keep the tip load as low as possible to produce high resolution image.

## 6. General tips to achieve atomic resolution

Atomic resolution images can be obtained by controlling tip-surface interactions as discussed above. In addition to tip-surface interactions, the following suggestions can be made to achieve atomic resolution:

- Use sharper tips. Weih *et al.* (Weihs *et al*., 1991) showed by calculations that the lateral resolution increased by a factor of 4 by reducing the tip radius from 200 to 20 nm. The sharper tip also reduces the adhesion force between a tip and the surface, which also decrease the tip load.
- Use stiffer tips. The elastic modulus could be increased by using a stiffer tip to achieve a smaller contact area between a tip and the surface. The smaller contact area between a tip and the surface is desired so as to realize only few atoms in contact. Ideally, a single atom of the tip should interact with each surface atom to obtain atomic resolution.
- Reduce tip load. By applying the cantilever bending force, the contact area between a tip and the surface could be reduced by lowering the tip load.
- Reduce adhesion. The work of adhesion can be minimized by immersing the tip and sample in liquid.

## 7. Artifacts and reproducibility

The topographs obtained by AFM should be reproducible and represent the real surface structure of the sample. Artifacts at the atomic scale are topographic features by which uncertainties and errors enter the surface structure determination. There are numerous

types of AFM artifacts, including missing atoms/molecules/vacancies, ghost atoms, and fuzzy steps etc. Most artifacts are caused by multiple-tip surface contacts and high tip loads. Ideally, a single atom tip interacts with the surface to obtain atomically resolved topographs. In reality, however, the structure, geometry, and surface chemistry of the AFM tips are usually poorly defined. During imaging, the AFM tip may get deformed and cause multiple point contacts. It is therefore highly desirable to monitor the structural and chemical modification of the tip before and after experiments. Equally, the low tip load is desirable for achieving high resolution atomic images. Ohnesorge and Binnig (Ohnesorge & Binnig, 1993) have demonstrated the dramatic change in topograph by carefully controlling the tip-surface interaction. Sokolov and Henderson (Sokolov & Henderson, 2000) also showed that an increased tip load destroys the atomically resolved images determined from the vertical force contrast and only improves lattice resolution images determined from the friction forces. Cleveland *et al.* (Cleveland *et al.*, 1995) also showed through atomic imaging of calcite and mica surfaces in water, that surface atoms could only be unambiguously identified when the tip load was attractive. It is thus highly recommended that one be cautious in interpreting AFM images before systematic studies of the tip load effect are carried out.

The AFM images should show the real surface structure and be reproducible. The surface structure should remain unchanged with varying probes, scanning directions, different location on the same surface, different sample of same material, tip-surface forces, and even different instruments and techniques if possible.

Finally, more confidence in the recorded AFM topographs will be gained if the same surface can be analyzed with other techniques such as STM, high resolution transmission electron microscopy, x-ray crystallography etc. Electron microscopy requires complex surface preparation procedures, but they are free from artifacts introduced in AFM images. These alternative techniques may compliment AFM in obtaining and verifying the atomic images.

## 8. Case study: Crystal lattice imaging of silica face and alumina face of kaolinite

Kaolinite naturally exists as pseudo-hexagonal, platy-shaped, thin particles generally having a size of less than one micron extending down to 100 nm. The crystallographic structure of kaolinite suggests that there should be two types of surface faces defined by the 001 and the 00$\underline{1}$ basal planes. In this way, one face should be described by a silica tetrahedral surface and the other face should be described by an aluminum hydroxide (alumina) octahedral surface as shown in figure 1. The objective of this case study is to demonstrate the bi-layer structure of kaolinite – a silica tetrahedral layer and an alumina octahedral layer, through atomic resolution obtained using AFM.

### 8.1 Materials and methods

#### 8.1.1 Sample preparation

A clean English kaolin (Imerys Inc., UK) was obtained from the St. Austell area in Cornwall, UK. The sample was cleaned with water and elutriation was used to achieve classification at a size of less than 2 μm. No other chemical treatment was done. Further details about the kaolinite extraction and preparation are given in the literature (Bidwell *et al.*, 1970).

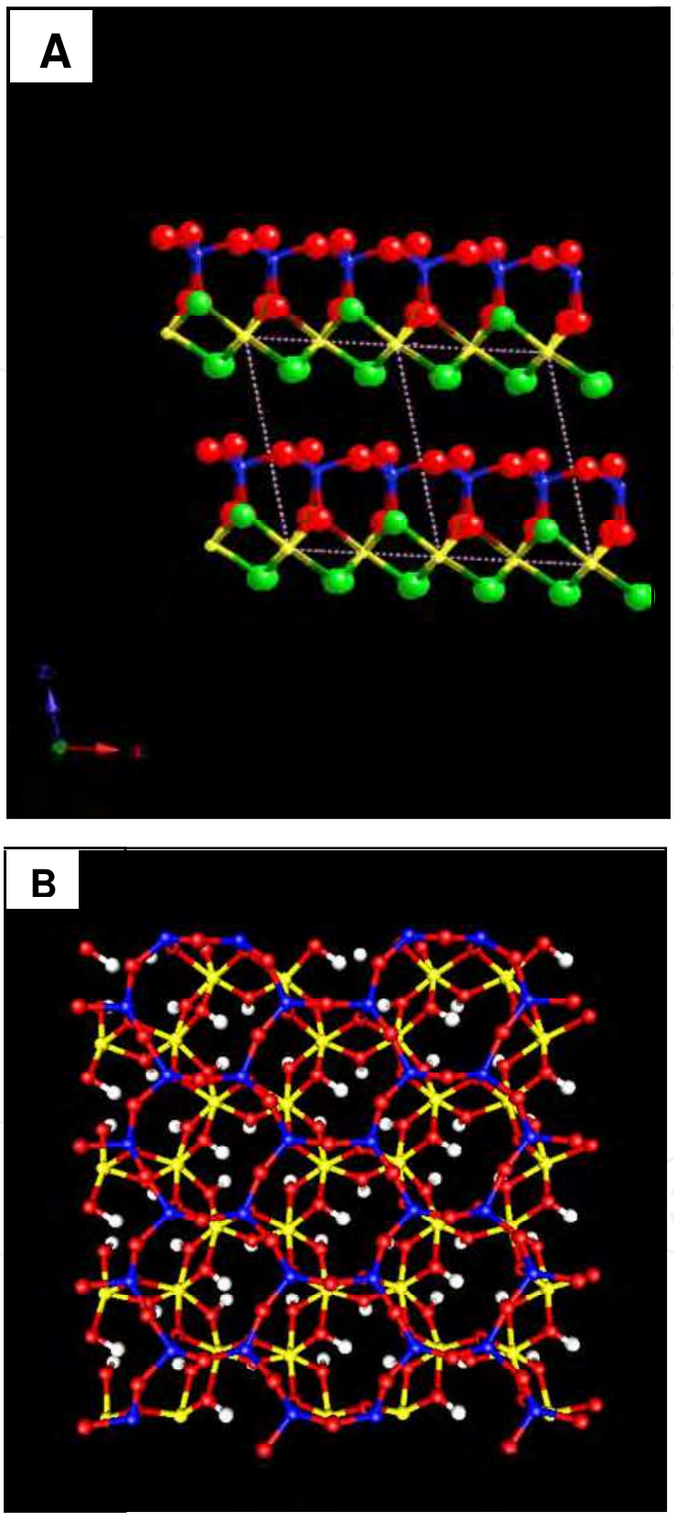


Fig. 1. Side view (A) and Top view (B) of kaolinite (001) surface structure. The silica tetrahedra (red: oxygen, blue: silicon) and alumina octahedra (yellow: aluminum, green: hydroxyl) bilayers thought to be bound together via hydrogen bonding are illustrated in (A).

The kaolinite suspension (1000 ppm) was prepared in high purity Milli-Q water (Millipore Inc.) with a resistivity of 18.2 MΩ-cm. The pH was adjusted to 5.5 using 0.1 M HCl or 0.1 M KOH solutions.

### 8.1.2 Substrate preparation

Two substrates – a mica disc (ProSciTech, Queensland, Australia) and a fused alumina substrate (Red Optronics, Mountain View, CA), were used to order the kaolinite particles (Gupta & Miller, 2010). The kaolinite particle suspension (1000 ppm) was sonicated for 2 minutes, and about 10 μl of the suspension was air-dried overnight on a freshly cleaved mica substrate under a petri-dish cover in a laminar-flow fume hood. In this way, the kaolinite particles attach to the mica substrate with the alumina face down exposing the silica face of kaolinite, as shown from previous surface force measurements (Gupta & Miller, 2010), i.e., the positively charged alumina face of kaolinite is attached to the negatively charged mica substrate.

The fused alumina substrate was cleaned using piranha solution (a mixture of sulfuric acid and hydrogen peroxide in a ratio of 3:1) at $120^0$C for 15 minutes, followed by rinsing with copious amounts of Milli-Q water, and finally blown dry with ultra high purity $N_2$ gas. A 10 μl kaolinite suspension was applied to the alumina substrate and dried in the same manner as the mica. It was found that the alumina face of kaolinite was exposed on the fused alumina substrate based on previous surface force measurements (Gupta & Miller, 2010), i.e., the negatively charged silica face of kaolinite is attached to the positively charged fused-alumina substrate.

The samples were prepared the night before AFM analysis and stored in a desiccator until their use. Just prior to the AFM experiments, the substrates were sonicated for a minute in Milli-Q water to remove loosely adhered kaolinite particles, washed with Milli-Q water, and gently blown with $N_2$ gas before AFM investigation. All substrates were attached to a standard sample puck using double-sided tape.

### 8.1.3 Atomic Force Microscopy

A Nanoscope AFM with Nanoscope IV controller (Veeco Instruments Inc., Santa Barbara, CA) was used with an E-type scanner. Triangular beam silicon nitride ($Si_3N_4$) cantilevers (Veeco Instruments Inc., Santa Barbara, CA), having pyramid-shaped tips with spring constants of about 0.58 N/m, were used. The cantilevers were cleaned using acetone, ethanol, water in that order, and gently dried with ultra high purity $N_2$ gas. The cantilevers were subsequently cleaned in a UV chamber for 30 minutes prior to use. The substrates were loaded on AFM equipped with a fluid cell. The contact mode imaging was done in Milli-Q water. The AFM instrument was kept in an acoustic and vibration isolation chamber. The imaging was commenced 30 minutes after sample loading to allow the thermal vibration of the cantilever to equilibrate in the fluid cell. First, an image of the particles was obtained at a scan rate of 1 Hz and scan area of 1 μm. Subsequently, the atomic resolution imaging was completed using the zoom-in and offset feature of the Nanoscope vs. 5.31R1 software (Veeco Instruments Inc., Santa Barbara, CA) to scan an area of 12 nm on the particle surface. The atomic imaging was obtained at a scan rate of 30 Hz at scan angle of $80^0$–$90^0$ with very low

integral and proportional gain (0.06). The online filters (low pass and high pass) were turned off during the online crystal lattice imaging.

During offline image processing, flattening and low pass filtering were applied to obtain clear images using Nanoscope vs. 5.31R1 software. The images were further Fourier-filtered (2D FFT) to obtain the crystal lattice images using SPIP software (Image Metrology A/S, Denmark).

## 8.2 Results and discussion

In order to obtain the crystal lattice imaging of the silica face and alumina face of kaolinite, the scanner was first calibrated using a mica substrate. Figure 8.2 presents the crystal lattice imaging of mica, which shows the height image, fast-Fourier transform (FFT) spectra and the FFT transformed height image. In order to make sure that the image is real, the imaging was acquired from other locations on the mica substrate and also with varying scan size and scan angle. The repeated pattern of dark and light spots was reproducible and the dark spots observed were scaled appropriately with the scan size and angle. The images showed some drift in both x and y direction during imaging. The dark spots in Figures 8.2C and 8.2D correspond to a hole surrounded by the hexagonal lattice of oxygen atoms. The light spots are attributed to the three-surface oxygen atoms forming a $SiO_4$ tetrahedron or pairs of $SiO_4$ tetrahedra forming a hexagonal ring-like network. Similar images were reported for the 1:1 type clay mineral, lizardite (Wicks *et al.*, 1992) and other 2:1 type clay minerals (Drake *et al.*, 1989; Hartman *et al.*, 1990; Sharp *et al.*, 1993) from AFM observations on a single crystal. The fast-Fourier transform showed the intensity peaks of oxygen atoms arranged in a hexagonal ring network (see Figure 8.2B). The crystal lattice spacing between neighboring oxygen atoms was calculated as 0.51 ± 0.08 nm, from the average of 10 neighboring atoms. This is in very good agreement with the literature value of 0.519 nm (Wicks *et al.*, 1993).

Figure 8.3 shows an image of a kaolinite particle on a mica substrate. The image shows the platy nature and the pseudo-hexagonal shape of the kaolinite particle. The scanning was sequentially zoomed on the particle. Figure 8.4 shows the crystal lattice imaging of the silica face of a kaolinite particle on the mica substrate. The flattening and low pass filtering was applied to the height image in an offline mode (see Figure 8.4B). The FFT spectra showed the similar intensity of peaks of oxygen atoms arranged in a hexagonal ring network as observed for the mica substrate. As expected, the silica face of kaolinite showed the similar hexagonal ring-like network of oxygen atoms as observed on the mica substrate (compare Figure 8.2D and Figure 8.4D). Note that the scan scale for the image of the silica face of kaolinite was twice that used for the mica substrate (12 nm vs. 6 nm), which shows the reproducibility of the crystal lattice images obtained on different substrates. The crystal lattice spacing between neighboring oxygen atoms was calculated as 0.50 ± 0.04 nm, from the average of 10 neighboring atoms. This lattice spacing is in good agreement with 0.53 nm as reported in the literature (Kumai *et al.*, 1995).

The crystal lattice imaging of the alumina face of kaolinite on a fused alumina substrate is shown in Figure 8.5. The FFT spectra shows the intensity peaks of the hydroxyl atoms forming a hexagonal ring network similar to that obtained on the silica face of kaolinite (see Figure 8.5C). Notice that the hexagonal ring of hydroxyls shows the inner hydroxyl in the center of the ring instead of a hole as observed for the silica face of kaolinite and mica

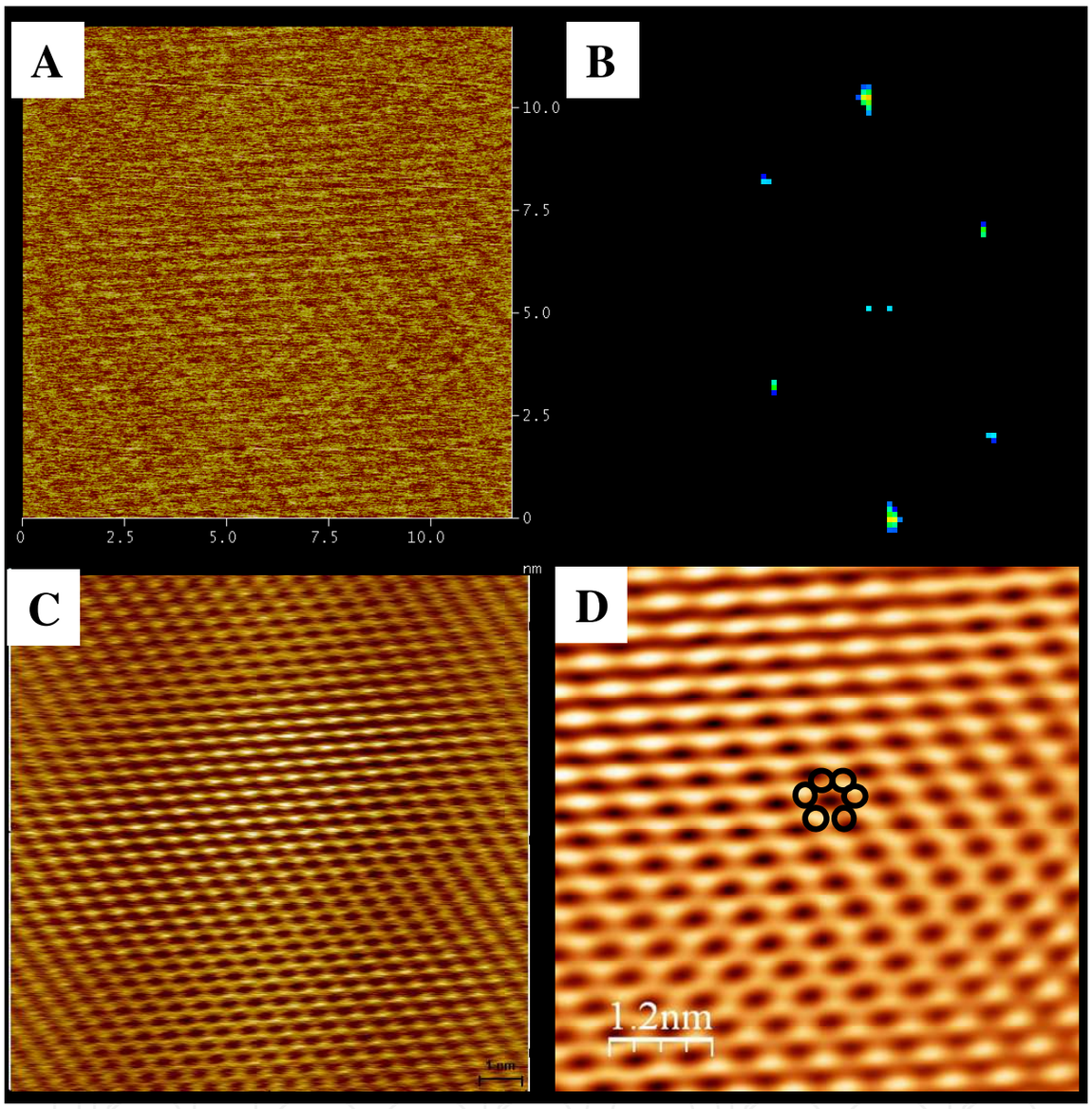


Fig. 2. Crystal lattice imaging of mica substrate showing (A) Flattened height image, (B) FFT spectra, (C) FFT transformed flattened height image, and (D) Zoomed-in image of (C) of scan area of 36 nm². The six light spots in (D) show the hexagonal ring of oxygen atoms around the dark spots representing a hole. Adapted from (Gupta *et al.*, 2010).

substrates (compare Figure 8.2D, Figure 8.4D, and Figure 8.5D). The image shown in Figure 8.5D is similar to the octahedral sheet of lizardite (Wicks *et al.*, 1992), the internal octahedral sheets of micas and chlorite (Wicks *et al.*, 1993), and the brucite-like layers of hydrotalcite (Cai *et al.*, 1994). The octahedral sheet of kaolinite consists of a plane of hydroxyls on the surface. The average hydroxyl-hydroxyl distance of the octahedral sheet is 0.36 ± 0.04 nm which is in reasonable agreement with the literature value of 0.29 nm (Wyckoff, 1968). For a kaolinite pellet, Kumai *et al.* (Kumai *et al.*, 1995) observed the distance between the hydroxyl atoms as 0.33 nm.

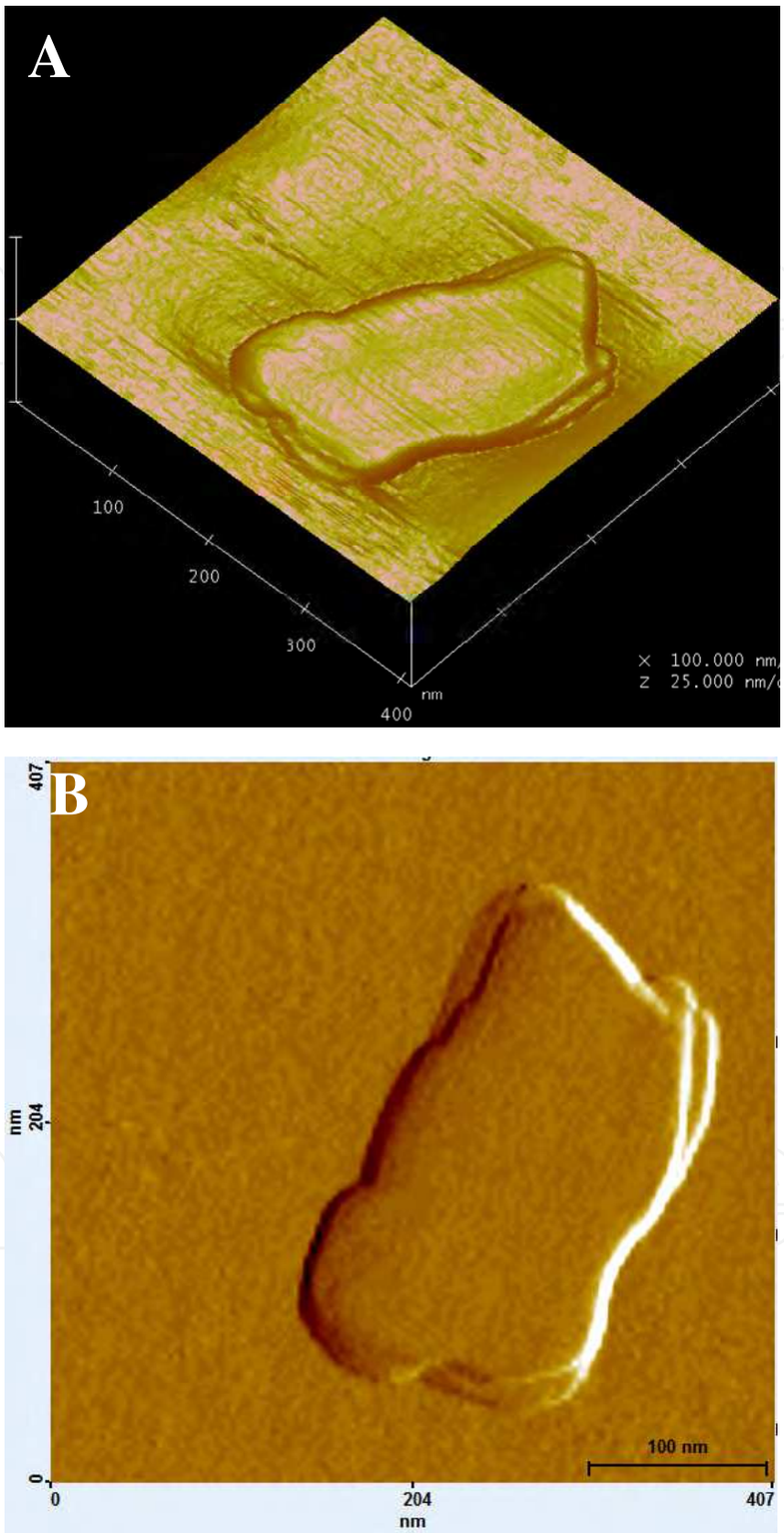


Fig. 3. (A) Topography, and (B) Deflection images of kaolinite particle on the mica substrate. Adapted from (Gupta *et al.*, 2010).

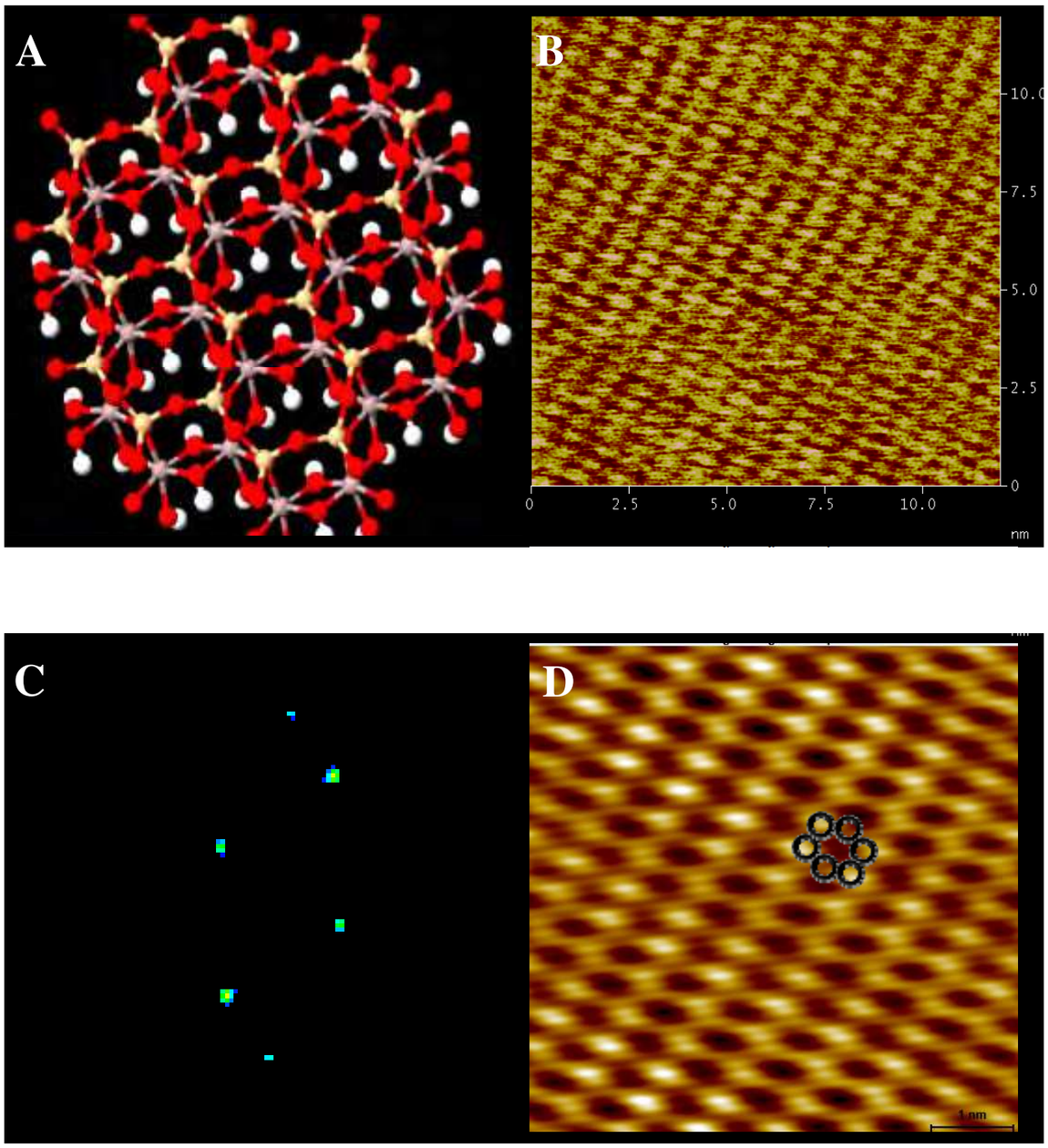


Fig. 4. Crystal lattice imaging of the silica face of kaolinite showing (A) Theoretical atomic lattice structure, (B) Flattened-low pass filtered height image, (C) FFT spectra, and (D) FFT transformed flattened-low pass filtered height image of scan size 36 nm². The six black circles in (D) show the hexagonal ring of oxygen atoms around the dark spots representing a hole. Adapted from (Gupta *et al.*, 2010).

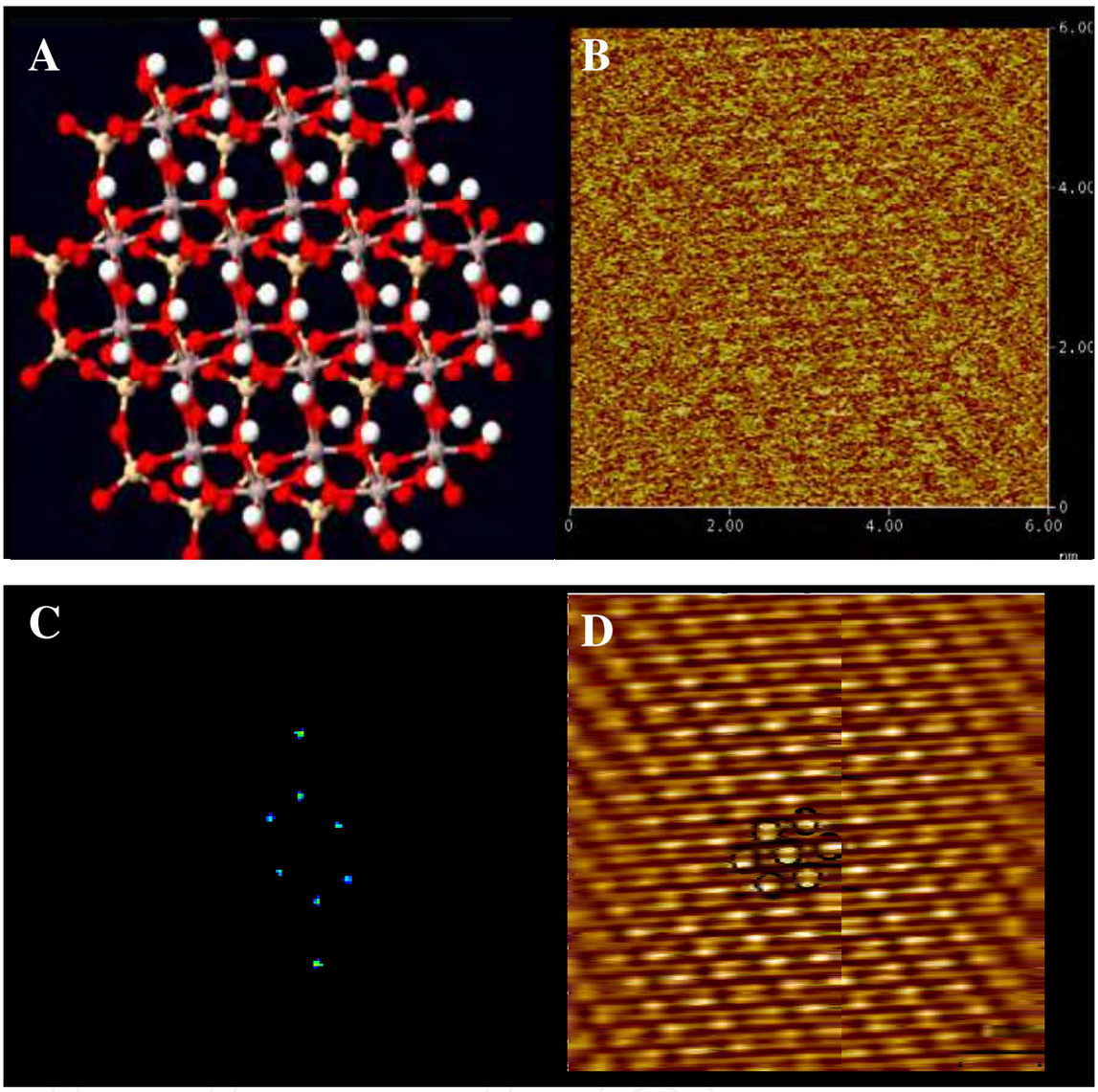


Fig. 5. Crystal lattice imaging of the alumina face of kaolinite showing (A) Theoretical atomic lattice structure, (B) Flattened-low pass filtered height image, (C) FFT spectra, and (D) FFT transformed flattened-low pass filtered height image of (B). The seven black circles in (D) show the hexagonal ring of hydroxyl atoms with a central inner hydroxyl atom. Adapted from (Gupta *et al.*, 2010).

## 9. Conclusions

For the last two decades, AFM has been established as an important tool for the study of surfaces. AFM produces information with minimal surface preparation that is not matched by other techniques. The quality of images has increased, as our understanding of the theory of the interaction of the tip and the sample. Atomic resolution images recorded on a variety of samples such as natural minerals, synthetic materials, zeolites, biological samples etc. have established the AFM as the microscope for the atomic scale.

Looking ahead, we must face several challenges to produce fast and reproducible atomic resolution images. One should be skeptical of high resolution topographs, and do diligent work in reporting data. The image acquisition procedures and filtering routines discussed in this chapter should be applied judiciously. One should be aware of artifacts introduced during real-time image acquisition or post processing should be dealt with cautiously, and must be reported. Probes play a key role in realizing high resolution topographs. The benefits of sharper tips are numerous, such as smaller contact area and reduced long range forces. Most conventional tips are made from silicon nitride and silicon. Polymers or diamond tips have also used in some applications (Beuret *et al.*, 2000). Recent developments in producing nano-tips through whiskers or carbon fiber may find potential application in AFM for high resolution images (Marcus *et al.*, 1989; Marcus *et al.*, 1990).

Recent developments on cantilever dynamic studies (Holscher *et al.*, 2006; Strus *et al.*, 2005) and new experimental techniques, such as Q-control (Ebeling *et al.*, 2006; Okajima *et al.*, 2003) and higher order vibration imaging (Martinez *et al.*, 2006) will very likely make AFM a powerful tool for high resolution characterization in the future. Despite recent developments in AFM instrumentation for precise control of tip movement, it is still highly desirable to confirm the reliability of AFM topographs with complimentary techniques such as transmission electron microscopy (Matsko, 2007). We can conclude that AFM is a powerful instrument, and could be used for studying a variety of surfaces.

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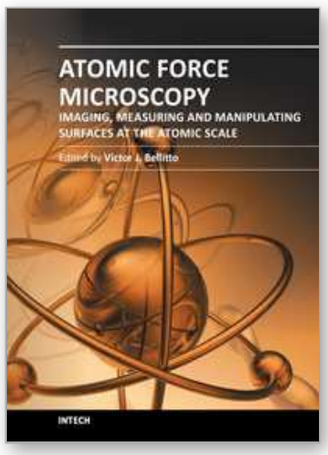


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With the advent of the atomic force microscope (AFM) came an extremely valuable analytical resource and technique useful for the qualitative and quantitative surface analysis with sub-nanometer resolution. In addition, samples studied with an AFM do not require any special pretreatments that may alter or damage the sample and permits a three dimensional investigation of the surface. This book presents a collection of current research from scientists throughout the world that employ atomic force microscopy in their investigations. The technique has become widely accepted and used in obtaining valuable data in a wide variety of fields. It is impressive to see how, in a short time period since its development in 1986, it has proliferated and found many uses throughout manufacturing, research and development.



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